Microscopic theory of reversible pressure broadening in hole-burning spectra of impurities in glasses

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(Received 13 September 1988, accepted 22 November 1988)

Recently, Sesselmann *et al.* [Phys. Rev. B **36**, 7601 (1987)] have examined the effect of pressure changes on hole-burning spectra of dye molecules in polymer glasses, finding that the hole shift and broadening are linear in the pressure change and its magnitude, respectively. We develop a statistical, microscopic theory of this effect, and of the inhomogeneous line shape itself. In the limit that the density of solvent perturbers becomes large, the general theory predicts that both the inhomogeneous line shape and the hole shape after a pressure change will be Gaussian, in qualitative agreement with experiment. By considering a specific model for the solute–solvent interaction, we then provide a quantitative analysis of the experiments that shows that the pressure broadening is due to changes in the local environment of each chromophore. As a further test of the theory, we make a prediction as to the frequency dependence of the pressure-dependent hole shift, which can be easily tested by experiment.

I. INTRODUCTION

The study of the structure and dynamics of glasses is an important problem in condensed matter physics and chemistry. Experimentally, this study often involves the use of dilute concentrations of dye molecules embedded in the host glass matrix. The problem then becomes one of extracting information about the glass from the changes in the spectroscopy of the guest molecules induced by the presence of the glassy solvent. These solvent effects can be divided into two classes: inhomogeneous effects arising from the distribution of solute environments, and homogeneous effects due to the dynamic fluctuations of each solute environment about its "equilibrium" state.

Up until now, the bulk of experimental and theoretical efforts have been directed at the study of the homogeneous solvent effects. In some crystalline systems and in all glassy systems, the optical linewidth of the dye is dominated by inhomogeneous broadening, so the major task of experiments that seek to study the homogeneous effects is to somehow "cut away" at the inhomogeneous line to expose the "bare" homogeneous one. This can be done either directly by photochemical or photophysical hole burning[1,2] or indirectly by means of the time-domain photon echo technique.[2,3] These experiments, with their subsequent theoretical analyses, have added to our understanding of the dynamics of the glass state, especially in providing some evidence for the existence of low-lying local excitations usually referred to as two-level systems (TLS),[4] which are believed to dominate the homogeneous broadening (and therefore, the dynamics of the glass solvent matrix) at very low temperatures.

In the above studies, the presence of the inhomogeneous contribution to the line shape is, for the most, part a nuisance that only serves to obscure the homogeneous line shape. These inhomogeneous effects are, however, interesting in their own right, being indicators of the degree of structural disorder present in the system under study. Recently, Sesselmann *et al.*[5] have conceived of and performed a series of innovative experiments that provide a sensitive probe into the nature of inhomogeneous solvent effects. The experiments utilize the technique of photochemical hole burning, which, as mentioned above, was developed to study homogeneous broadening. The experiments are easily summarized. First, using a laser, a narrow hole is burned in the inhomogeneous line shape of a particular dye molecule optical transition, which is broadened and shifted due to the presence of the glass matrix. The hole in the line shape arises because the laser alters photochemically a significant population of those dye molecules with transition frequencies within the bandwidth of the laser. The transition frequencies of these molecules are changed significantly enough so that they no longer contribute to the inhomogeneous line under study. This leaves a "hole" in the line shape at the laser frequency. After the hole is burned, the external hydrostatic pressure on the system is changed. The hole responds to the pressure change by both broadening and shifting in frequency. The shift is due to the change in the average solvent density and the broadening comes about from breaking of the accidental transition frequency degeneracy among otherwise distinct solute environments. A closely related effect, involving accidental degeneracies in the absolute energy distribution of a single state, has been discussed phenomenologically by Lee, Walsh, and Fayer[6] and will also be considered from a more microscopic viewpoint in a future paper by the present authors.[7]

The polymer–glass systems studied were: polyethylene (PE), polystyrene (PS), and polymethylmethacrylate (PMMA). All three polymers were doped with a dilute concentration of the dye molecule free base phthalocyanine (H_2Pc). The doping concentrations were on the order of 10^{-4} moles of H_2Pc per mole of solvent monomer. The inhomogeneously broadened line shape under study was due to the $S_1 \leftarrow S_0$ optical transition of the dye. For all three polymer solvents, the shift in the center frequency of the hole was found to be linear in the pressure change over the range of pressure studied (red shifting for increasing pressures and blue shifting for decreasing pressures). The broadening was

 0021-9606/89/063274-08$02.10

found to be linear in the *magnitude* of the pressure change, i.e., the hole broadened for both pressure increases and decreases. Both effects were observed to be completely reversible in all systems studied.

These experiments are much more sensitive probes of the pressure dependence of inhomogeneous solvent effects than previous experiments, which focus on the pressure dependence of the *entire* inhomogeneous line shape, for two reasons. First, the pressure changes necessary to produce detectable changes in the holes are orders of magnitude smaller (MPa vs GPa) than those necessary to shift detectably the entire line.[8] Second, the degree to which the holes are broadened is a good indication of the degree of microscopic disorder in the glass structure, and provides information that is not obtainable from the previous studies.

With these experiments as motivation, we have developed a microscopic theory of inhomogeneous broadening based upon the statistical method originally developed by Markov.[9] Markov's method in its standard form has been used by several workers in the calculation of inhomogeneous line shapes (see the review of Stoneham[10]). In our theory, we extend this formalism to construct a general theoretical framework within which both the inhomogeneous line shape *and* the pressure effects described above can be discussed and predicted for systems of the type studied in the experiments of Sesselmann *et al.* The development of this theory is outlined in Sec. II.

In order to use the theory to analyze experimental data for a specific glass/dye system, a microscopic model for the solvent–solute interaction and structure must be constructed. In the analysis of their experiments, Sesselmann *et al.* assumed that the inhomogeneous broadening is entirely due to long-ranged attractive induced-dipole/induced-dipole interaction between the solute and the solvent molecules. They also assumed that the solvent density is uniform outside a sphere centered at the solute molecule (taken to be spherical) and zero inside. Using a simple theory, they predicted a pressure dependence of the frequency shift of the holes, which is in reasonable agreement with their experimental results on the PE–, PS–, and PMMA–H_2Pc systems. However, the theory that they used in the calculation of the pressure shift was not general enough to enable the calculation of the pressure broadening. When the theory developed in Sec. II is applied to this model, we obtain a prediction for the pressure shift that is identical to theirs, but the pressure broadening of the holes is found to be zero—a result contrary to experiment. To remedy this problem, we have constructed another model of the solute–solvent interaction that includes long-range dispersion forces as well as short-range repulsive interactions. The details of the model are discussed in Sec. III. In Sec. IV, this model is analyzed using the extended theory and found to give results that are consistent with the experiments to within experimental error.

II. STATISTICAL THEORY OF INHOMOGENEOUS BROADENING AND REVERSIBLE PRESSURE EFFECTS

We consider a system consisting of a dilute concentration of solute molecules embedded in a glass of N solvent molecules. For a polymer glass, the solvent "molecules" are the monomeric units, or parts thereof, of the polymer. Each solvent molecule interacts with the ground electronic state of a solute molecule with a potential energy that depends upon the position (and possibly the orientation) of the solvent relative to the solute. When the solute is in an excited electronic state, in general there is a different interaction potential. If we denote the perturbation of the solute ground and excited state frequencies due to a single solvent molecule by $\nu_g(\mathbf{R})$ and $\nu_e(\mathbf{R})$, respectively, then the perturbed transition frequency is given by

$$\nu(\mathbf{R}) = \nu_e(\mathbf{R}) - \nu_g(\mathbf{R}) . \tag{1}$$

The vector $\mathbf{R}$ represents the position (and possibly the orientation) of the solvent molecule relative to the solute. The solvent–solute interactions are assumed to be pairwise additive so that the total perturbation of a given solute transition energy due to its solvent environment is simply the sum of the perturbations due to each individual solvent molecule. The solute–solute interaction is neglected by reason of the low solute concentration.

Each solute molecule occupies a different spatial position within the (disordered) glass and, therefore, experiences a different solvent environment. The inhomogeneous line shape arises as a consequence of this distribution of solvent environments, which we represent by the probability distribution $P(\mathbf{R}_1,...,\mathbf{R}_N)$, where $\mathbf{R}_i$ is the position vector of the ith solvent unit (from here on we assume that the solvent–solute interaction does not depend on the solvent orientation). This probability function is assumed to be normalized by

$$\int d\mathbf{R}_1 \cdots d\mathbf{R}_N P(\mathbf{R}_1,...,\mathbf{R}_N) = V^N , \tag{2}$$

where V is the volume of the system. In principle, once the function $\nu(\mathbf{R})$ and the distribution $P(\mathbf{R}_1,...,\mathbf{R}_N)$ are specified, the (normalized) inhomogeneous line shape, $I(\nu)$, can be calculated from the relation

$$I(\nu) = V^{-N} \int d\mathbf{R}_1 \cdots d\mathbf{R}_N P(\mathbf{R}_1,...,\mathbf{R}_N) \times \delta\left(\nu - \sum_{i=1}^{N} \nu(\mathbf{R}_i)\right) . \tag{3}$$

We now make the assumption that the position of each solvent molecule relative to a given solute is statistically independent of that of the other solvent molecules. This is probably the most serious of the approximations that make up the foundation of the theory. Mathematically, this means that the $(N+1)$-particle solute–solvent distribution function (N solvent molecules plus one solute molecule), $P(\mathbf{R}_1,...,\mathbf{R}_N)$, factors into a product of N two-particle solute–solvent distribution functions. If this solute–solvent distribution function is denoted by $g(\mathbf{R})$, then we have

$$P(\mathbf{R}_1,\mathbf{R}_2,...,\mathbf{R}_N) = g(\mathbf{R}_1)g(\mathbf{R}_2)\cdots g(\mathbf{R}_N) . \tag{4}$$

Replacing the δ function in Eq. (3) by its integral representation gives

$$I(\nu) = (2\pi)^{-1} \int_{-\infty}^{\infty} dx\, e^{i\nu x} \left[V^{-1} \int d\mathbf{R}\, g(\mathbf{R}) e^{-i\nu(\mathbf{R})x} \right]^N . \tag{5}$$

Defining a new function $J(x)$ by

$$J(x) = \int d\mathbf{R}\, g(\mathbf{R}) [1 - e^{-i\nu(\mathbf{R})x}] , \tag{6}$$

then gives

$$I(\nu) = (2\pi)^{-1} \int_{-\infty}^{\infty} dx\, e^{i\nu x} \left[1 - \frac{\rho}{N} J(x) \right]^N , \tag{7}$$

where $\rho = N/V$ is the bulk single-particle number density of the solvent molecules. Since we are dealing with macroscopic sample sizes, we want to take the limit $N \to \infty$ subject to the constraint that ρ remains constant, i.e., the thermodynamic limit. Using the well known relation

$$\lim_{n \to \infty} [1 + z/n]^n = e^z \tag{8}$$

gives the result

$$I(\nu) = (2\pi)^{-1} \int_{-\infty}^{\infty} dx\, e^{i\nu x} e^{-\rho J(x)} . \tag{9}$$

This is the standard statistical method result for the inhomogeneous line shape.[10]

The analysis of the pressure tuning experiments of Sesselmann *et al.*[5] requires a more detailed description of the inhomogeneous solvent effects than simply a specification of the line shape. The quantity that is required to calculate the shift and broadening of a distribution of frequencies selected from within the inhomogeneous band is the conditional probability function $f(\nu'|\nu;\Delta p)$. This function is the probability that if a solute molecule has transition frequency ν at the initial experimental pressure, then after the pressure of the sample has been changed by Δp, the new transition frequency is ν'. Given some initial distribution of frequencies, $i(\nu)$ (such as that selected out by the laser through the hole-burning process), the new distribution after the pressure change Δp, $i(\nu';\Delta p)$, is then given by

$$i(\nu';\Delta p) = \int_{-\infty}^{\infty} d\nu f(\nu'|\nu;\Delta p) i(\nu) . \tag{10}$$

The calculation of the function $f(\nu'|\nu;\Delta p)$ from the microscopic properties of the system can be accomplished by an extension of the statistical method formalism. An equation for $f(\nu'|\nu;\Delta p)$ similar to Eq. (3) for the line shape can be written as

$$f(\nu'|\nu;\Delta p) = \frac{1}{I(\nu) V^N} \int d\mathbf{R}_1 \cdots d\mathbf{R}_N\, P(\mathbf{R}_1,\ldots,\mathbf{R}_N) \times \delta\left(\nu - \sum_{i=1}^{N} \nu(\mathbf{R}_i) \right) \times \delta\left(\nu' - \sum_{i=1}^{N} \nu'(\mathbf{R}_i;\Delta p) \right) , \tag{11}$$

where the function $\nu'(\mathbf{R};\Delta p)$ is the value of the solute transition frequency perturbation after the Δp pressure change, due to a solvent molecule that was initially at $\mathbf{R}$. Implicit in this formulation of $f(\nu'|\nu;\Delta p)$ is the assumption that the solvent matrix is rigid and that the only effect of the pressure change is a (not necessarily homogeneous or isotropic) compression or dilation. This is a reasonable assumption due to the glassy nature of the solvent, the extremely low temperatures at which the experiments are performed, and the observed reversibility of the pressure effects.

By replacing the δ functions in Eq. (11) by their integral representations and following the same series of assumptions and mathematical manipulations by which Eq. (9) is derived from Eq. (3), the following relation for the conditional probability function is obtained:

$$f(\nu'|\nu;\Delta p) = \frac{1}{4\pi^2 I(\nu)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx\, dy\, e^{i\nu x} e^{i\nu' y} e^{-\rho j(x,y)} , \tag{12}$$

where

$$j(x,y) = \int d\mathbf{R}\, g(\mathbf{R}) (1 - e^{-i\nu(\mathbf{R})x} e^{-i\nu'(\mathbf{R};\Delta p)y}) . \tag{13}$$

The pressure changes involved in the pressure tuning experiments are small enough that the observed pressure shifts are linear in Δp (the observed broadenings are linear in $|\Delta p|$). With this in mind, the function $\nu'(\mathbf{R};\Delta p)$ can be linearized about $\Delta p = 0$ to give

$$\nu'(\mathbf{R};\Delta p) = \nu(\mathbf{R}) + \alpha(\mathbf{R}) \Delta p . \tag{14}$$

If the assumption is made that the compression or dilation due to the pressure change is both isotropic and homogeneous, the linear coefficient in Eq. (14) becomes

$$\alpha(\mathbf{R}) = -\frac{R}{3} \frac{\partial \nu(\mathbf{R})}{\partial R} \kappa , \tag{15}$$

where $\kappa = -V^{-1}(\partial V/\partial p)$ is the bulk isothermal compressibility of the solvent and R is the magnitude of $\mathbf{R}$. Substituting Eqs. (14) and (15) into Eqs. (12) and (13) gives

$$f(\nu'|\nu;\Delta p) = \frac{1}{4\pi^2 I(\nu)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dy\, dz \times e^{i\nu z} e^{i(\nu' - \nu)y} e^{-\rho \tilde{j}(y,z)} , \tag{16}$$

where

$$\tilde{j}(y,z) = \int d\mathbf{R}\, g(\mathbf{R}) [1 - e^{-i\nu(\mathbf{R})z} e^{-i\alpha(\mathbf{R})y\Delta p}] . \tag{17}$$

Equations (6) and (9), together with Eqs. (16) and (17), provide a straightforward procedure for calculating both the inhomogeneous line shape $I(\nu)$ and the pressure kernel $f(\nu'|\nu;\Delta p)$, once the details of the system are specified. However, the use of these equations as they stand is complicated by the fact that the integrals involved cannot, in general, be evaluated analytically. This limits the ease in which the theory can be applied to specific systems. There is, fortunately, an approximation which leads to simple expressions for both $I(\nu)$ and $f(\nu'|\nu;\Delta p)$ and is accurate for the types of experimental situations toward which this work is directed. This approximation is based on the observation

that for sufficiently large values of the density ρ, the integrand in Eq. (9) is dominated by the values of x for which $J(x)$ is well approximated by the first two terms in its Taylor series about $x=0$. This expansion gives

$$J(x) = iAx + \tfrac{1}{2}Bx^2 + \ldots, \tag{18}$$

where

$$A = \int d\mathbf{R}\, g(\mathbf{R})\nu(\mathbf{R}) \tag{19}$$

and

$$B = \int d\mathbf{R}\, g(\mathbf{R})[\nu(\mathbf{R})]^2 . \tag{20}$$

When this expression for $J(x)$ is substituted into Eq. (9), the following Gaussian expression for the inhomogeneous line shape is obtained:

$$\begin{aligned} I(\nu) &= (2\pi\sigma_s^2)^{-1/2}\exp\left[-\frac{(\nu-\nu_s)^2}{2\sigma_s^2}\right], \\ \nu_s &= \rho A , \\ \sigma_s &= (\rho B)^{1/2} , \end{aligned} \tag{21}$$

where ν_s is the solvent shift and σ_s is the width of the inhomogeneous line shape. The quantity σ_s is related to the experimentally measured full-width half-maximum (FWHM) of the inhomogeneous line Γ_s by

$$\sigma_s = \frac{\Gamma_s}{2\sqrt{2\ln 2}} . \tag{22}$$

Thus, the line shape is completely determined within this approximation by the first two moments of $g(\mathbf{R})$, both of which can be calculated easily. This tendency toward a Gaussian line shape at high densities is a manifestation of the central limit theorem.

By similar arguments and expansions, the pressure kernel, $f(\nu'|\nu;\Delta p)$, can also be approximated by a Gaussian in this high density limit

$$f(\nu'|\nu;\Delta p) = \{2\pi[\Delta\sigma(\Delta p)]^2\}^{-1/2} \times \exp\left[-\frac{[\nu'-\nu-\Delta\nu(\nu,\Delta p)]^2}{2[\Delta\sigma(\Delta p)]^2}\right], \tag{23}$$

where the pressure shift $\Delta\nu(\nu,\Delta p)$ is given by

$$\Delta\nu(\nu,\Delta p) = \rho\left[A' + \frac{C(\nu-\nu_s)}{\sigma_s^2}\right]\Delta p \tag{24}$$

and the pressure broadening $\Delta\sigma(\Delta p)$ is given by

$$\Delta\sigma(\Delta p) = \sqrt{\rho\left[B' - \frac{\rho C^2}{\sigma_s^2}\right]}\,|\Delta p| . \tag{25}$$

The quantities ν_s and σ_s are as in Eq. (21). The other quantities A', B', and C are the moments

$$A' = \int d\mathbf{R}\, g(\mathbf{R})\alpha(\mathbf{R}) , \tag{26}$$

$$B' = \int d\mathbf{R}\, g(\mathbf{R})[\alpha(\mathbf{R})]^2 , \tag{27}$$

$$C = \int d\mathbf{R}\, g(\mathbf{R})\alpha(\mathbf{R})\nu(\mathbf{R}) . \tag{28}$$

The pressure broadening FWHM, $\Delta\Gamma(\Delta p)$ is related to $\Delta\sigma(\Delta p)$ in the same way that Γ_s is related to σ_s [see Eq. (22)].

If the original hole were a delta function centered at ν, then the observed hole shape after the pressure change would be given by the kernel $f(\nu'|\nu;\Delta p)$. However, since the original hole has a nonzero width, the observed hole shape after the pressure change is given by the convolution in Eq. (10). In the actual experiments,[5] for most pressure changes, the width of the kernel is substantially larger than the width of the original hole, so that the observed hole shape is, in fact, given approximately by the kernel. Therefore, the functions $\Delta\nu(\nu,\Delta p)$ and $\Delta\Gamma(\Delta p)$ are the principal quantities measured by the experiments.

The above Gaussian approximation is valid for sufficiently large solvent densities. The applicability of this approximation to the systems to which this study is addressed will be assumed for the present, and justified *a posteriori* in Sec. IV. Here we note simply that both the experimental inhomogeneous line shapes and pressure broadened holes are, in fact, approximately Gaussian.

Before proceeding further, it is interesting to take note of two general properties of the pressure broadening and shift as described by Eqs. (23)–(28). First, the pressure broadening is proportional to the *absolute value* of the pressure change. Thus, a narrow hole burned in the inhomogeneous line will broaden for both pressure increments and decrements. This effect is observed experimentally, and is consistent with the idea that the broadening is a result of breaking the accidental transition frequency degeneracy of otherwise different solvent environments by action of the change in pressure. Second, the pressure shift $\Delta\nu(\nu,\Delta p)$, which is proportional to the pressure change as observed experimentally, is also a function of the specific frequency within the inhomogeneous line at which the original hole is burned. Thus, a hole burned in the blue side of the distribution will have a pressure shift that is different from that of a hole burned to the red of center, even though the two holes are subjected to identical pressure changes. This is in contrast to the pressure broadening, for which no such variation is predicted. It will be shown in Sec. IV that this variation in the shift is predicted to be significant (10%–20%) for the PS–, and PE–H_2Pc systems. In the actual experiments performed, the holes were burned at the center of the inhomogeneous line shape. In light of this fact, the pressure shift (unless otherwise indicated) will be assumed to be evaluated at the center of the line shape, $\nu=\nu_s$, and the frequency argument of $\Delta\nu$ will be dropped. It is interesting to note that, as long as the Gaussian approximation holds, the pressure shift of a hole burned at the center of the line shape is the same as the pressure shift of the center of the inhomogeneous line itself. This means that, in principle, the quantity $\Delta\nu(\Delta p)$ could be obtained from an experiment measuring only the response of the entire line to an external pressure change, although the low sensitivity of such an experiment limits its practicality for this purpose.

III. A SIMPLE MODEL FOR THE POLYMER GLASS–DYE MOLECULE SYSTEM

The application of the theory as outlined in the previous section to a specific model requires the specification of four quantities: the transition frequency perturbation $\nu(\mathbf{R})$, the solute–solvent two-particle distribution function $g(\mathbf{R})$, the solvent number density ρ, and the solvent isothermal compressibility κ. The latter two are bulk thermodynamic quantities and can be obtained from the literature. Specification of the first two for a specific experimental system is not as straightforward.

Consider first the problem of determining $\nu(\mathbf{R})$ for the polymer–dye systems currently under study. From Eq. (1) it can be seen that this requires the knowledge of both the ground state and excited state solute–solvent potentials. These are not well known even for the very simplest real systems, much less for the complex systems on which this study is focused. Given this lack of hard facts about the potentials, the job of the theorist is to use general qualitative properties of intermolecular potentials together with some intuition about the geometry of these polymer–dye systems to construct a caricature of $\nu(\mathbf{R})$ that is hoped to contain enough of the physics to give reasonable results.

When both the solute and solvent are nonpolar, the interaction between them in the limit of large solvent–solute separation is given to a good approximation by the familiar induced-dipole/induced-dipole inverse-sixth-power attraction. This is true whether the solute is in the ground or in the excited state. Since this interaction is proportional to the product of the solute and solvent polarizabilities, and the excited solute state is generally more polarizable than is the ground state, the function $\nu(\mathbf{R})$ then takes on the following form at large R:

$$\nu(\mathbf{R}) = -\frac{c}{R^6}, \tag{29}$$

where c is an undetermined positive constant. Equation (29) gives only the long-range behavior of $\nu(\mathbf{R})$. Both the ground and excited state potentials will become repulsive at short range as the solute and solvent electron clouds begin to overlap.

In the analysis of their experiments, Sesselmann *et al.*[5] devise a simple theory for the pressure shift $\Delta\nu$ that is based on the assumption that the inhomogeneous line shape is due only to the long-range attractive part of $\nu(\mathbf{R})$ given in Eq. (29). They also assume that the compressibility in the neighborhood of the solute can be different from the bulk value. If, however, one assumes that they are identical, as in the present formalism, then their expression for the pressure shift,

$$\Delta\nu(\Delta p) = 2\nu_s\kappa\Delta p, \tag{30}$$

is the same as that obtained by using Eqs. (15), (24) (with $\nu = \nu_s$), (26), and (29), together with

$$g(\mathbf{R}) = \begin{cases} 1 & \text{if } R \geqslant R_c \\ 0 & \text{if } R < R_c \end{cases}. \tag{31}$$

Equation (30) is in reasonable agreement with the experimental results on the PE–, PS–, and PMMA–H_2Pc systems.[5]

A major failure of this model becomes apparent when the pressure broadening $\Delta\Gamma(\Delta p)$ is calculated via Eq. (25). Although experimentally a substantial broadening of the holes is seen, this model gives a $\Delta\Gamma(\Delta p)$ that is identically zero! This result, which is independent of the Gaussian approximation and independent of the $g(\mathbf{R})$ chosen, is true for any $\nu(\mathbf{R})$ of the inverse power form:

$$\nu(\mathbf{R}) \propto \frac{1}{R^n}. \tag{32}$$

Physically, this result is due to the fact that, for such models, every member of a degenerate set of solvent environments responds in exactly the same way to a change in pressure, thus the energy degeneracy is not broken and no broadening is observed.

It is clear, given the failure of this simple model based only on dispersion forces to predict pressure broadening, that a more realistic model potential must be constructed. The potential should include, at least in a rudimentary way, the repulsive short-range interactions as well as the required long-range dispersive behavior. Considering first the ground electronic state solute–solvent interaction, the most obvious choice is a potential based on the familiar Lennard-Jones (LJ) form

$$\nu_g(\mathbf{R}) = 4\epsilon_g\left[\left(\frac{\sigma_g}{R}\right)^{12} - \left(\frac{\sigma_g}{R}\right)^{6}\right], \tag{33}$$

where ϵ_g is the depth of the potential well and σ_g is a characteristic length scale. However, as a model for the polymer glass/dye system, this potential still has one major drawback. In general, the dye molecule is much bigger than the perturbing solvent monomer units. Since σ_g in Eq. (33) represents the sum of the solute and solvent effective radii, if the size disparity is large, the range of the potential would be much larger than the diameter of a solvent molecule. This is qualitatively incorrect since the range of the repulsive interaction is physically only about one solvent radius measured from the surface of the solute molecule, regardless of the size ratio.

To correct this defect in the potential, we propose a modified Lennard-Jones potential that differs from the standard form [Eq. (33)] in that it is shifted along the radial direction by an amount R_0

$$\nu_g(\mathbf{R}) = \begin{cases} 4\epsilon_g\left[\left(\frac{\sigma}{R-R_0}\right)^{12} - \left(\frac{\sigma}{R-R_0}\right)^{6}\right] & \text{if } R \geqslant R_0 \\ \infty & \text{if } R < R_0 \end{cases}. \tag{34}$$

This form of this potential was inspired by the work of Berne and Gay.[11] This potential is now qualitatively correct with regard to the above length scale problem. It should also be noted that with this potential σ can be interpreted as the solvent diameter, while $R_0 + \sigma/2$ is the solute radius. Clearly, when $R_0 = 0$, this shifted LJ form reduces to the standard form, reflecting equality in the solute and solvent sizes.

To keep matters reasonably simple, we assume that the excited electronic state solute–solvent potential is *also* given by Eq. (34), but with ϵ_g replaced by ϵ_e (with $\epsilon_e > \epsilon_g$).

Therefore, the frequency shift $\nu(\mathbf{R})$ is *also* given by Eq. (34), but with ϵ_g replaced by $\epsilon \equiv \epsilon_e - \epsilon_g > 0$. We note that this simple model involving only a change of ϵ in going from the ground to the excited state potentials, as well as a model involving only a change in σ, have been previously studied by Herman and Berne in their Monte Carlo simulations of the electronic spectrum of Br_2 in liquid Ar.[12]

Next, the problem of specifying a model solute–solvent $g(\mathbf{R})$ must be addressed. Real $g(\mathbf{R})$'s for systems like those presently under study are very complex and not well characterized. Therefore, given the relative simplicity of the theory, it seems logical to assume the simplest $g(\mathbf{R})$ possible that is consistent with the ground state potential as specified in Eq. (34):

$$g(\mathbf{R}) = \begin{cases} 1 \text{ if } R \geqslant R_c + R_0 \\ 0 \text{ if } R < R_c + R_0 \end{cases} . \tag{35}$$

This $g(\mathbf{R})$ is a step function like the one used by Sesselmann *et al.* [Eq. (31)], except it reflects the shift in the potential due to R_0.

IV. RESULTS AND COMPARISON TO EXPERIMENT

The pressure tuning experiments directly measure four properties of the inhomogeneous line; ν_s, Γ_s, $\Delta\Gamma(\Delta p)$, and $\Delta\nu(\Delta p)$. The calculation of these four quantities for the model system described in the previous section requires the specification of six parameters: ρ, κ, σ, R_0, R_c, and ϵ. For a specific system, the first two parameters, ρ and κ, are readily obtainable from the literature (the number density ρ of the solvent monomer units is determined from the experimental mass density ρ_m). In choosing the appropriate value of σ for PE and PS, we have used the effective LJ diameters of methane and benzene, respectively, extracted from viscosity or second virial coefficient data. The literature values of ρ_m,[13] κ,[14] and σ,[15] as well as $\rho^* \equiv \rho\sigma^3$, are listed in Table I for polyethylene (PE) and polystyrene (PS). Polymethylmethacrylate (PMMA) was excluded from this analysis because it is a polar solvent and, as such, does not satisfy the assumptions implicit in the construction of the model potential.

Specifying the value of ϵ is problematic. In constructing the model potential function, we have made an ansatz as to its form but our lack of knowledge about the true ground and excited state potentials prevents us from making an *a priori* estimation of the proper energy scale. However, the need for prior specification of ϵ can be avoided by reducing the set of four experimental energy shifts and broadenings to a set of three dimensionless ratios as follows:

$$\beta = \frac{\Delta\nu(\Delta p)}{\nu_s \kappa \Delta p} , \tag{36}$$

TABLE I. Thermodynamic parameters for polyethylene (PE) and polystyrene (PS).

	ρ_m (g cm^{-3}) (Ref. 11)	κ(M Pa^{-1}) (Ref. 12)	σ(Å) (Ref. 13)	$\rho^* = \rho\sigma^3$
PE	0.855	0.141×10^{-3}	3.822	2.053
PS	1.04	0.179×10^{-3}	5.27	0.8815

$$\gamma = \frac{\Delta\Gamma(\Delta p)}{\Gamma_s \kappa |\Delta p|} , \tag{37}$$

$$\delta = \frac{\nu_s}{\Gamma_s} . \tag{38}$$

These ratios are independent of the energy scale, and therefore, ϵ. The values of these ratios as well as the original four experimental quantities[5] are given for PE and PS in Table II.

The remaining two parameters of our model potential, the shift R_0 and the $g(\mathbf{R})$ cutoff R_c, are, like ϵ, not subject to *a priori* estimation as a result of our lack of knowledge about the actual microscopic structure of the solvent–solute system. Unfortunately, unlike the situation with ϵ, the lack of knowledge about these two fundamental length scales cannot be swept under the rug by a judicious manipulation of the experimental results. We must therefore view them as adjustable parameters.

We now have two adjustable parameters and three experimentally determined dimensionless ratios for each polymer/dye system. It is then possible to use two of the experimental ratios together with Eqs. (19)–(21) and (24)–(28) to fix the values of the two parameters via a two-dimensional fit. The model, now fully specified, can then be used to predict the value of the remaining ratio, which can be compared to the experimental value. Which two of the three ratios are used to determine the adjustable length scales is a subjective choice. We have chosen to use β and δ for this purpose, leaving γ as the quantity to be predicted by the model. We make this choice for the following reason: β could, in principle, be determined from a standard measurement of the pressure dependence of the entire inhomogeneous line shape, and δ simply reflects the inhomogeneous line shape at a single pressure, whereas, the pressure broadening ratio γ is a quantity that can only be determined by experiments that can probe the internal structure of the inhomogeneous band, such as the pressure tuning experiments that are the subject of this work. This fact, for us, makes γ the more interesting quantity.

The results of the two-dimensional fit for R_0 and R_c for the two systems PE and PS are displayed in Table III. The error bars in the fitted values of the two length scale parameters are due to the experimental error in the ratios β and δ. The spatial integrals involved in the evaluation of Eqs. (19), (20) and (26)–(28) were performed numerically. First, considering the fitted R_0 values, we see that for the effective radius of the solute molecule H_2Pc, $R_0 + \sigma/2$, we obtain 8.52 ± 1.18 Å and 6.3 ± 0.5 Å for PE and PS, respectively. Given the very crude approximation of replacing the flat H_2Pc molecule[16] by a sphere, these values for the effective radius (and the discrepancy between them) seem reasonable. Second, the values of the $g(\mathbf{R})$ cutoff R_c that we obtained are approximately equal to σ, which is consistent with the form of the ground-state potential.

Also in Table III are shown the predicted values of the broadening parameter γ, which are 4 ± 1 and 1.97 ± 0.40 for PE and PS, respectively. These should be compared with the experimental values (from Table II) of 3.67 ± 0.69 and

TABLE II. Experimental data (Ref. 5) for polyethylene (PE) and polystyrene (PS).

	ν_s (cm^{-1})	Γ_s (cm^{-1})	$\frac{\Delta\nu(\Delta p)}{\Delta p}\left(\frac{cm^{-1}}{M\,Pa}\right)$	$\frac{\Delta\Gamma(\Delta p)}{\lvert\Delta p\rvert}\left(\frac{cm^{-1}}{M\,Pa}\right)$	β	γ	δ
PE	-690 ± 10	116 ± 10	-0.18 ± 0.01	0.06 ± 0.01	1.85 ± 0.11	3.67 ± 0.69	-5.95 ± 0.52
PS	-742 ± 10	276 ± 10	-0.22 ± 0.01	0.12 ± 0.01	1.66 ± 0.08	2.43 ± 0.22	-2.69 ± 0.10

2.43 ± 0.22, respectively. This agreement between the theoretical and experimental pressure broadening parameter signifies that our simple theoretical model does provide a reasonable first approximation to the experimental systems under study.

Finally, from the magnitude of the solvent shifts we can extract the energy parameters ϵ, which are also shown in Table III. Although it is difficult to comment meaningfully about these parameters, we note simply that since ϵ is the difference in the excited and ground state well depths, one might expect them to be smaller than typical (ground state) Lennard-Jones well depths, which they are.

The above calculations were performed using the Gaussian approximation to the broadenings and shifts as outlined in Sec. II. The applicability of this approximation to the present systems has yet to be demonstrated. As a test, we calculate, using the parameters given in Tables I and III, the predicted inhomogeneous line shape using both the Gaussian approximation [Eqs. (19)–(21)] and the exact Eqs. (6) and (9). The results of this comparison for both the PE– and PS–H_2Pc systems are displayed in Figs. 1 and 2, respectively. From Fig. 1 it is seen that the Gaussian approximation is almost exact for the case of PE. In the case of PS (Fig. 2), the difference between the two curves is greater than in PE (due to the lower reduced density of PS), but the Gaussian approximation is nevertheless quite good.

As discussed in Sec. II, the theory predicts a variation in the pressure shift as a function of the frequency ν within the line shape at which the hole is burned. Now that the parameters of the model have been completely specified for both polymer systems under study, it is possible to use Eq. (24) to predict the magnitude of this variation. This procedure, for PE and PS, gives

$$\frac{\Delta\nu(\nu,\Delta p)}{\Delta p} \approx -0.18\left(\frac{cm^{-1}}{M\,Pa}\right) + 1.27 \times 10^{-4}(M\,Pa^{-1})(\nu + 690\ cm^{-1})(PE) \quad (39)$$

and

$$\frac{\Delta\nu(\nu,\Delta p)}{\Delta p} \approx -0.22\left(\frac{cm^{-1}}{M\,Pa}\right) + 1.72 \times 10^{-4}(M\,Pa^{-1})(\nu + 749\ cm^{-1})(PS)\,. \quad (40)$$

The above expressions give predicted variations of $\Delta\nu$ over the FWHM of 8% and 22% for PE and PS, respectively. Therefore, an interesting test of the theory would be an accurate experimental determination of this variation for the two systems studied here. In fact, a similar variation for a PMMA-pentacene polymer/dye system, may have already been seen.[17]

TABLE III. Calculated parameters for polyethylene (PE) and polystyrene (PS).

	R_0/σ	R_c/σ	γ	ϵ (cm^{-1})
PE	1.73 ± 0.31	1.028 ± 0.010	4 ± 1	6 ± 2
PS	$0.7\ \pm0.1$	1.045 ± 0.012	1.97 ± 0.40	36 ± 4

V. CONCLUSION

Dilute concentrations of dye molecules have been used to probe spectroscopicly the structure of glasses. One manifestation of the glass structure is the inhomogeneous line shape of the dye, which gives the probability distribution of the dye transition frequency as perturbed by the glass. Another manifestation involves the response of a subset of dye molecules with a specific transition frequency to an external perturbation. The pressure-dependent hole-burning experiments of Sesselmann *et al.* provide an example of the latter.

In this paper, we have set out to develop a microscopic theory of inhomogeneous broadening in glasses that is gen-

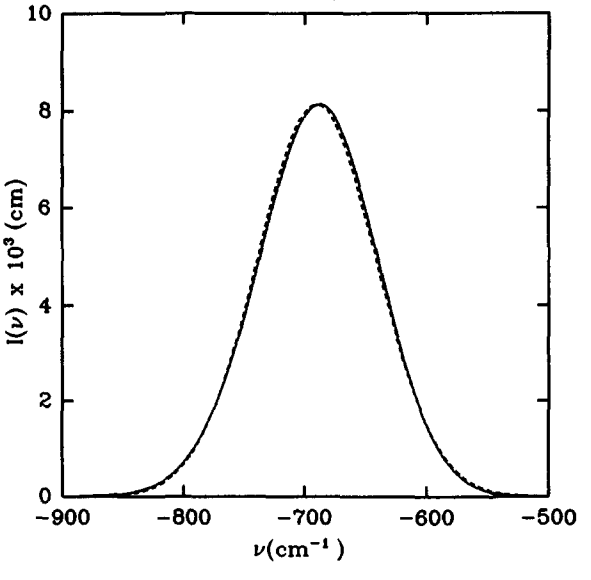

FIG. 1. Comparison of the exact (solid line) and Gaussian (dotted line) theoretical predictions for the inhomogeneous line shape for the PE/H_2Pc system.

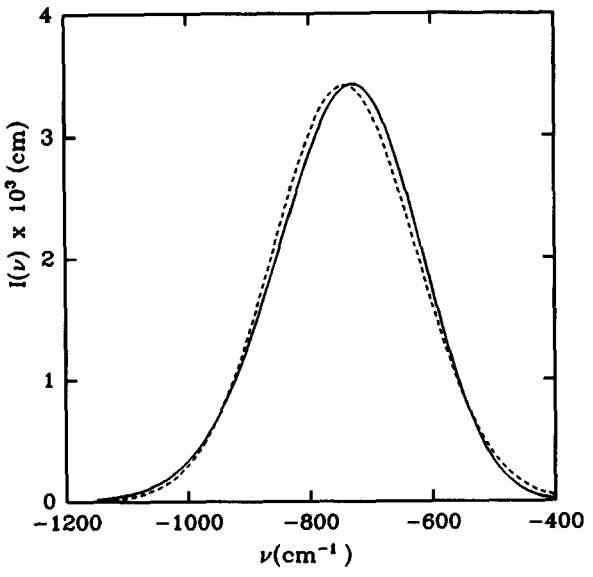

FIG. 2. Same as Fig. 1 except for the PS/H_2Pc system.

eral enough to predict the results of the pressure tuning experiments of Sesselmann *et al.* as well as the inhomogeneous line shape itself. One of the important ingredients in the theory is the assumption that the solvent (glass) molecules are randomly distributed around each chromophore. Another is the form of the chromophore transition frequency perturbation due to a single solvent molecule.

In the analysis of their experiments, Sesselmann *et al.* have focused on the role of the long-range contribution to this transition frequency perturbation. With this picture, they were able to explain successfully the pressure dependence of the hole frequency shifts. Adapting this idea to our more general theoretical framework shows that the long-range perturbation is in fact primarily responsible for this frequency shift, as well as the overall inhomogeneous line shape, but cannot explain the pressure broadening of the holes. This shows that this latter effect is particularly interesting, because it is evidently a probe of the local structure and interactions of the glass/dye system.

To understand the pressure broadening of the holes, we have considered a model for the solute transition frequency perturbation that has both long- and short-range contributions, and have been able to explain the experimental observations. The physical interpretation of the hole shift and broadening is the following: The initial hole-burning event selects out a set of dye molecules that have different environments, although they have (accidentally) the same transition frequency. On the average, when the environments are perturbed by changing the pressure, the transition frequency shifts due to a density change of the sample that modifies the many long-range interactions. The broadening of the holes arises from the fact that the environment of each chromophore changes differently due primarily to the short-range interactions. Thus the accidental degeneracy of the original set of laser-selected dye molecules is broken by the pressure change.

Finally, since the statistical theory involving a random distribution of solvent molecules around each chromophore can adequately describe the experimental data, we are inclined to conclude that the presence of the impurity does not induce any significant ordering of the solvent, and in that sense may be considered a useful probe for determining the local structure and dynamics of the glass in the absence of impurities.

ACKNOWLEDGMENTS

We thank Thomas Sesselmann and Dietrich Haarer for sending us a preprint of Ref. 5 and for the helpful discussions that initiated this research, and also we acknowledge Bruce Berne for his illuminating remarks on intermolecular potentials. This research is supported by the National Science Foundation under Grant Nos. DMR86-03394 and CHE83-51207, and by the Alfred P. Sloan and Camille and Henry Dreyfus Foundations.

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